

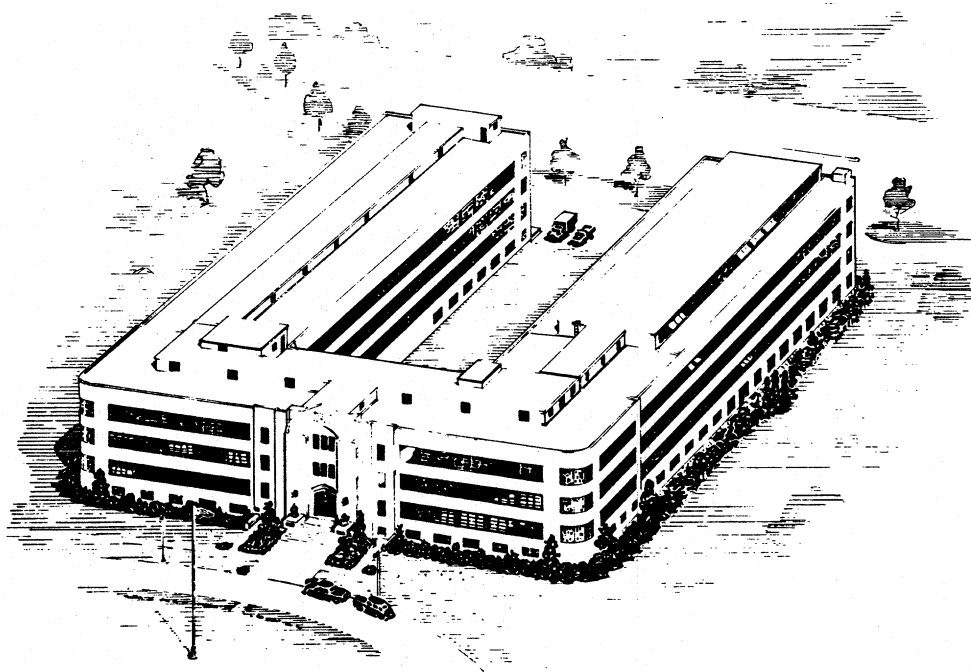
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UNITED STATES DEPARTMENT OF AGRICULTURE
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VINYL PLASTICS MODIFIED WITH CHEMICALS FROM ANIMAL FATS

COPOLYMERS OF VINYL CHLORIDE AND VINYL STEARATE

*William S. Port, Edmund F. Jordan, Jr., William E. Palm, Lee P. Witnauer,
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INTRODUCTION

As part of a broad program on the utilization of polymerizable monomers prepared from animal fats (1 7), vinyl stearate has been copolymerized with monomers whose homopolymers normally require plasticization in the expectation of obtaining modified polymers in which the softening agent is integrally bound (internal plasticization). It was expected that in some respects internally plasticized copolymers would be superior to resins plasticized in the usual way in that the "plasticizer" cannot migrate or evaporate.

Since vinyl stearate can be prepared from low-cost stearic acid and acetylene, (12-15 cents and 12 cents per pound, respectively) in more than 90 per cent yield by a simple process, a low price for this monomer may be expected if a large market develops. To determine what useful products can be prepared from vinyl stearate and to aid in estimating the volume of vinyl stearate that such products might require, various copolymers of vinyl stearate and commercially available monomers have been prepared, and their general physical properties have been measured. This report describes the preparation and physical properties of copolymers of vinyl chloride containing from about 10 to 45 weight per cent of vinyl stearate.

MONOMERS

Vinyl stearate was prepared by vinylation of stearic acid with acetylene in the presence of a zinc stearate catalyst at 165° C. and 200 p.s.i.g. A commercial grade of stearic acid that assayed at least 95 per cent stearic acid and contained less than 1 per cent unsaturates was used. The vinyl stearate met the following specifications: melting point, 34° C. minimum; refractive index, n_D^{40} 1.4419 minimum to 1.4425 maximum; when heated for 4 hours in a nitrogen atmosphere at 70± 2° C. in the presence of 0.25 weight

/1 THIS IS PAPER VIII IN THE SERIES 'POLYMERIZABLE DERIVATIVES OF LONG-CHAIN FATTY ACIDS'. PAPER VII IS REFERENCE 7.

per cent of benzoyl peroxide, it yielded a polymer having a minimum refractive index, n_D^{55} 1.4540.

From a practical point of view, the important specification for the stearic acid is its low content of unsaturates. Other work with copolymers from the vinyl esters of a variety of saturated acids and vinyl chloride indicated that copolymers with properties similar to those given in this report can be obtained from commercial mixtures of palmitic and stearic acids having a similar low content of unsaturates. In the present work, a relatively pure vinyl stearate was used to reduce the number of variables.

Vinyl chloride was obtained in cylinders from commercial sources and was flash distilled to separate it from inhibitors. The standard of purity was based on this polymerizability test: a minimum of 90 per cent is polymerized by the suspension method (one part of vinyl chloride to two parts of 1 per cent Aerosol OT² solution) in 48 hours at 50° C. with 0.15 per cent benzoyl peroxide as the initiator.

PREPARATION OF THE COPOLYMERS

Suspension (also known as bead or pearl) and emulsion polymerization techniques are the principal methods used in commercial practice. Therefore these methods were used in the present work. The copolymers on which the physical properties were measured were prepared by the recipes given below. Other recipes can undoubtedly be developed, but the properties of the copolymers obtained may differ in some respects.

Suspension Polymerization

The following general recipe was used:

Monomer mixture, grams	200
Aerosol OT ² or polyvinyl alcohol solution (1 per cent), ml.	400
Benzoyl peroxide, mole per cent	0.039
Temperature, °C.	50 + 3°
Reaction time, hours	48
Yield, per cent	Approx. 90

Table 1 lists the specific monomer mixtures, the weights of initiator used, and the vinyl stearate content of the copolymers obtained. A convenient laboratory container for the polymerizations is a heavy-walled, crown-capped bottle (for example, a 32-ounce soft drink bottle).

² REFERENCE TO COMMERCIAL PRODUCTS IN THIS REPORT IS NOT INTENDED TO BE A RECOMMENDATION OF THESE PRODUCTS BY THE UNITED STATES DEPARTMENT OF AGRICULTURE OVER OTHERS NOT MENTIONED.

When the time allotted for the reaction had elapsed, the excess vinyl chloride was allowed to evaporate. Any emulsion present was broken by the addition of salt, and the copolymer was separated and washed free of dispersant. Any unused vinyl stearate was extracted with boiling methanol, and the copolymer was dried. (The extraction step is probably unnecessary when the conversion is high.)

TABLE 1. - VINYL CHLORIDE - VINYL STEARATE COPOLYMERS PREPARED IN SUSPENSION

<u>Monomer mixture</u>		<u>Initiator</u>	<u>Copolymer</u>
<u>Vinyl stearate</u> grams	<u>Vinyl chloride</u> grams	<u>Benzoyl peroxide</u> grams	<u>Vinyl stearate</u> per cent
22.6	177.4	0.276	9.7
41.5	158.5	0.253	18.0
71.2	128.8	0.216	32.7
93.5	106.5	0.191	41.7

The number average degree of polymerization of the copolymers prepared by the suspension technique was about 500.

Emulsion Polymerization

The following general recipe was used to prepare emulsion copolymers:

Monomer mixture, grams	200
Tergitol Penetrant 4 ² (100% basis), grams	10
Water, grams	390
Potassium persulfate, mole per cent	0.039
Temperature, ° C.	50° ± 1°
Reaction time, hours	24
Yield, per cent	95-97

Table 2 lists the specific monomer mixtures, the weights of initiator used, and the amount of salt required to give a stable latex in the preparation of copolymers of the compositions shown.

TABLE 2. - VINYL CHLORIDE - VINYL STEARATE COPOLYMERS PREPARED IN EMULSION

<u>Monomer Mixture</u>		<u>Salt</u>	<u>Initiator</u>	<u>Copolymer</u>
<u>Vinyl</u> <u>stearate</u>	<u>Vinyl</u> <u>chloride</u>	<u>Sodium</u> <u>chloride</u>	<u>Potassium</u> <u>persulfate</u>	<u>Vinyl</u> <u>stearate</u>
grams	grams	grams	grams	per cent
22.6	177.4	1	0.308	11.5
40.4	159.6	2	0.282	19.1
71.6	128.4	4	0.242	35.7
93.5	106.5	4	0.212	45.2

The salt content of the emulsifier solution has a critical effect on the stability of the emulsion formed, but some slight variation is permissible and probably depends on the (unknown) salt concentration of the commercial emulsifier solution. In some cases, a higher emulsifier content (e.g., 5 per cent) without additional salt also gave a stable latex.

The copolymers were recovered by freezing the latex and remelting the mixture. The products so obtained were easily filtered and washed free of emulsifier, in contrast with copolymers obtained by salt precipitation techniques. Any unused vinyl stearate was extracted with boiling methanol.

The number average degree of polymerization of copolymers prepared in emulsion was about 800.

PHYSICAL PROPERTIES

The copolymers are white, free-flowing fine powders or small white beads. Their solubility in the common organic solvents increases as the vinyl stearate content increases. Thus, whereas copolymers containing about 10 per cent vinyl stearate are soluble only in tetrahydrofuran and to a limited extent in ethylene chloride, methyl ethyl ketone, and methyl isobutyl ketone, copolymers containing 30 to 40 per cent vinyl stearate are readily soluble in these solvents and also in benzene, xylene, chlorobenzene, and chloroform. A 20 per cent solution of a copolymer containing about 30 per cent vinyl stearate can be prepared in equal parts of benzene and acetone. The copolymers are insoluble in alcohols and in straight chain aliphatic hydrocarbons.

Copolymers containing from 10 to 35 per cent vinyl stearate are not attacked by 1 per cent aqueous sodium hydroxide, 50 per cent aqueous ethanol and 3 and 30 per cent aqueous sulfuric acid in 11 days (8). A copolymer containing about 35 per cent vinyl stearate shows a 39 per cent increase in weight when immersed in cottonseed oil, but the copolymer containing only 10 per cent is not attacked.

Table 3 lists some of the thermal, tensile (9), and flexural properties of the copolymers prepared. It may be seen that as the vinyl stearate content increases, the tensile strength and the modulus of elasticity decrease and the per cent elongation increases. This resembles the changes observed with increasing external plasticizer content, but the shape of the stress-strain curve is different. The difference between the curves may be seen in Figure I in which "Tensilgrams" obtained on a Scott I.P.-4 tester are reproduced (without correction for the slight differences in specimen thickness). In the "Tensilgrams" for the vinyl stearate copolymers (curves 3-6), there is an initial high modulus, which is present even in the compositions that contain more than 40 per cent vinyl stearate (curves 5 and 6). This high initial modulus is observed in incompletely plasticized stocks (curve 2), but not in well-plasticized compositions (curve 1). The copolymers prepared in emulsion (curves 4 and 6) more nearly approximate externally plasticized stocks (curve 1) than do the copolymers prepared in suspension.

Figure II shows that similar differences appear in creep measurements (10). A commercial stock (VYDR) plasticized with 35 per cent tricresyl phosphate (curve 1) shows an initial high response to deformation, with little further, long-time creep. The copolymers of vinyl chloride and vinyl stearate that contain approximately 35 per cent vinyl stearate (curves 2 and 3) show a lower initial response but a greater long-time creep. A difference in creep behavior between copolymers prepared in emulsion (curve 2) and those prepared in suspension (curve 3) is also shown. The copolymer prepared in emulsion shows a slightly better initial response and less long-time creep. The copolymer containing 41 per cent vinyl stearate (curve 4) shows a high initial response and high long-time creep. Within the limits of the time of measurement and the stress imposed, there is complete dimensional recovery upon removal of the stress.

In studies on the effect of temperature on creep behavior (copolymer composition kept constant), the rate of change of creep with time increased with temperature, whereas in stocks externally plasticized with 25 or 35 per cent dioctyl phthalate or 35 per cent tricresyl phosphate, the slopes of the creep curves remained nearly constant. With 25 per cent tricresyl phosphate, however, a similar increase of slope with temperature was observed.

The magnitude of the thermal properties also decreases with increasing vinyl stearate content (Table 3). Of particular interest in fabrication is the lower milling temperature. In addition, a study of the change of bulk viscosity with temperature in which the parallel plate plastometer (11) was used revealed a smaller change in viscosity with temperature than was found with polyvinyl chloride plasticized with tricresyl phosphate or dioctyl phthalate. This characteristic is desirable in extrusion, calendering and similar operations when it is undesirable to have the fabricated article set rapidly.

In ultraviolet light stability tests, copolymers of vinyl chloride containing about 35 per cent vinyl stearate but with no stabilizer present did not darken until 70 hours of exposure; when a lead stabilizer was present, samples did not darken even after 90 hours. Commercial samples of plasticized polyvinyl chloride containing a lead stabilizer darkened considerably after 46 hours, with exudation of plasticizer.

The flexural strength and stiffness (12) also decrease with increasing vinyl stearate content. The similarity to externally plasticized stocks exists here, too. The copolymers prepared in emulsion show greater flexural stiffness at low temperature (39° F.) and decreased stiffness at room temperature (73° F.) than do the suspension copolymers. Qualitatively, it has been found that the emulsion copolymers show better recovery from extension. In studies of copolymers of vinyl chloride with other vinyl esters, it was found that copolymers of vinyl chloride with vinyl esters of fatty acids containing less than about twelve carbon atoms do not have desirable flexibility properties.

MODIFICATION OF COPOLYMERS

Plasticization and Blending

Flexible films can be prepared from copolymers containing 10 per cent vinyl stearate by plasticizing them with conventional plasticizers, such as dioctyl phthalate, or with less expensive plasticizers readily prepared from fats with which these copolymers, unlike polyvinyl chloride, are compatible. On the other hand, copolymers containing above about 30 per cent vinyl stearate form flexible films without addition of plasticizer.

Commercial polyvinyl chloride resins and vinyl chloride-vinyl stearate copolymers are compatible. The blends have lower tensile strength and stiffness and higher elongation than do copolymers with comparable vinyl stearate contents. Elastomers prepared from butadiene-acrylonitrile, butadiene-styrene, or acrylonitrile-butyl acrylate blend with copolymers of vinyl chloride-vinyl stearate. For example, a blend of 25 parts of a butadiene-acrylonitrile rubber and 100 parts of a vinyl chloride copolymer containing 32 per cent vinyl stearate gave a flexible film having a tensile strength of 1720 pounds per square inch, a 100 per cent modulus of 1020 pounds per square inch and an elongation of 330 per cent.

Cure and Reinforcement

Polyfunctional amines and polyfunctional amines plus sulfur can be used to cure copolymers of vinyl chloride and vinyl stearate at 300° F. to infusible, insoluble products. The cured copolymers can be released from the mold without cooling. Carbon black or silica fillers may be used to reinforce the cured or uncured copolymers. Table 4 shows the change in tensile properties with cure and loading for two copolymers. Although polyvinyl chloride and its copolymers with vinyl acetate can be similarly cured, the copolymers of vinyl chloride with vinyl stearate have the advantage of being millable at a temperature at which the rate of cure is negligible, and they can then be cured at a higher temperature.

TABLE 3

CHARACTERISTICS OF COPOLYMERS OF VINYL CHLORIDE AND VINYL STEARATE^{/1}

	Prepared in suspension				Prepared in emulsion			
Weight per cent vinyl stearate in copolymer	9.7	18.0	32.7	41.7	11.5	19.1	35.7	45.2
Heat distortion temperature, °C. (13)	55.5	44.4	33.1	---	---	---	---	---
Clash-Berg T _f , °C. (14)	41.7	27.0	7.6	9.7	41.3	26.5	1.8	-7.2
Milling temperature, °F.	250	210	200	180	280	220	200	150
Tensile strength, lbs./sq. in.	6000/2	4000/2	2400/3 1300/2	1840/3 780/2	5500/2	4200/3 3400/2	2200/3 1500/2	1600/3
Elongation, per cent	<30	30	200	260	---	65	310	340
100 per cent modulus	---	---	2000	1500	---	---	1800	1300
Modulus of elasticity (under tension)	372,000	228,000	19,600	---	342,000	212,000	4,300	---
Flexural strength, lbs./sq. in.	11,200	5,500	2,600	---	---	---	---	---
Modulus of elasticity (under flexure)	367,000	235,000	90,000	---	---	---	---	---
Flexural stiffness, lbs./sq in. at 73°F.	226,000	147,000	20,500	1,300	270,000	164,000	6,800	4,400
lbs./sq. in. at 39°F.	275,000	231,000	110,000	---	---	---	128,000	---

^{/1} FOR COMPARISON. SOME OF THE PHYSICAL PROPERTIES OF A COMMERCIAL VINYL CHLORIDE COPOLYMER CONTAINING 5 PER CENT VINYL ACETATE PLASTICIZED WITH 35 PER CENT DIOCTYL PHTHALATE WERE MEASURED: CLASH-BERG T_f, 27°C.; MILLING TEMPERATURE, 300°F.; TENSILE STRENGTH, 3040 LBS./SQ. IN.; 100 PER CENT MODULUS, 1290 LBS./SQ. IN.; ELONGATION 350 PER CENT; FLEXURAL STIFFNESS AT 73°F., 1060 LBS./SQ. IN.; AT 39°F., 5300 LBS./SQ. IN.

^{/2} ASTM DESIGNATION D638-52T EXCEPT THAT A BAR SPECIMEN 1" X 0.25" X 5" WAS USED.

^{/3} SCOTT I.P. 4 INCLINED PLANE TESTER AT A RATE OF LOADING OF 75 LBS./MIN. ASTM DESIGNATION D882-49T.

TABLE 4

CURE AND REINFORCEMENT OF VINYL CHLORIDE-VINYL STEARATE COPOLYMERS

	Copolymer A(41.2 per cent vinyl stearate)			Copolymer B(47.8 per cent vinyl stearate)		
	Tensile/ strength	100 per cent Modulus	Elongation	Tensile/ strength	100 per cent Modulus	Elongation
	Lbs./sq. in.		per cent	Lbs./sq. in.		per cent
Uncured, unreinforced	2205	1940	305	1385	1060	310
Cured, unreinforced	2390	1955	230	1650	1155	260
Uncured, HI-SIL, reinforced	2620	2455	190	1730	1500	240
Uncured, FURNEX, reinforced	2750	2560	160	1700	1365	180
Cured, HI-SIL, reinforced	2495	2350	175	1725	1410	170
Cured, FURNEX, reinforced	2880	---	100	1950	1740	110

/1 SCOTT I.P..4

RECIPE

COPOLYMER..	PARTS	100
STEARIC ACID..	PARTS	1
LEAD CARBONATE..	PARTS	3
REINFORCING AGENT..	PARTS	25 (WHEN REINFORCED)
TRIETHYLENETETRAMINE..	PARTS	4 (WHEN CURED)

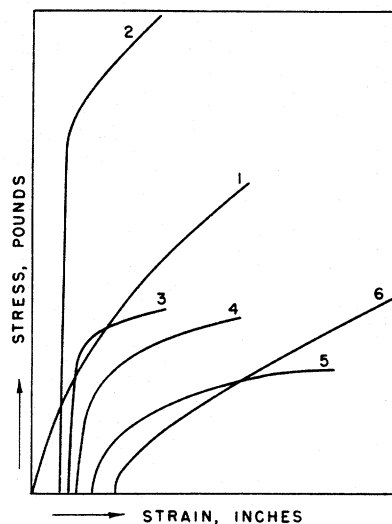


Figure 1. Tensile properties of copolymers of vinyl chloride and vinyl stearate.

KEY

1. Geon 101, 35 percent dioctyl phthalate. 2. Vinylite VYDR, 20 percent dioctyl phthalate. 3. Suspension copolymer, 32.3 percent vinyl stearate. 4. Emulsion copolymer, 35.6 percent vinyl stearate. 5. Suspension copolymer, 41.2 percent vinyl stearate. 6. Emulsion copolymer, 46.3 percent vinyl stearate.

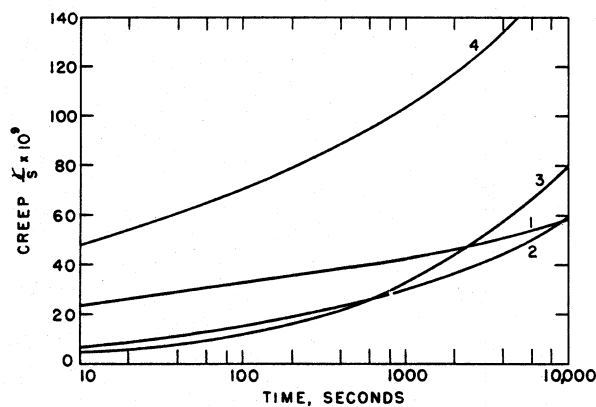


Figure 2.. Creep behavior of copolymers of vinyl chloride and vinyl stearate.

KEY

1. Vinylite VYDR, 35 percent tricresyl phosphate, 30° C.
2. Emulsion copolymer, 34.8 percent vinyl stearate, 31° C.
3. Suspension copolymer, 33.6 percent vinyl stearate 31° C.
4. Suspension copolymer, 41.2 percent vinyl stearate, 31° C.

SUGGESTED USES

The copolymers fall into two general categories. Copolymers that contain about 10 to 20 per cent of vinyl stearate are essentially rigid plastics. They appear to offer advantages for uses in which a low milling temperature and a low viscosity temperature coefficient are preferred. Suggested applications are plastic tubes, pipes, and other extruded forms, sheets for structural purposes, such as floor covering and wallboard, and specialty uses, such as phonograph records and toys.

Copolymers that contain about 30 to 45 per cent vinyl stearate resemble polyvinyl chloride resins that have been plasticized externally with about 25 to 35 per cent plasticizer. These copolymers should be of particular advantage where plasticizer loss by migration, extraction or evaporation must be avoided or where elimination of plasticizer odor is desirable. Applications that suggest themselves are coatings for wire, including protective sheathing for coaxial cable, protective coverings for varnished surfaces, fabric coatings, especially those subjected to repeated wiping or washing, such as automobile seat covers and table covers, and materials for food packaging. In uses where flexible polyvinyl chloride resins must be bonded to metals or other surfaces, the plasticizer may migrate to the adhesive and cause failure. Use of vinyl stearate-modified copolymers should avoid this difficulty.

Vinyl chloride-vinyl stearate copolymers to which plasticizers have been added may find use as flexible films or in plastisol compositions. Cured copolymers may find uses where an insoluble but flexible shape or coating is desired.

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SUMMARY

Copolymers of vinyl chloride that contain approximately 10 to 45 per cent vinyl stearate were prepared in suspension and in emulsion, and the tensile, flexural, viscosity, and low temperature properties were measured. The copolymers can be divided into two classes, rigid (low vinyl stearate content) and internally plasticized or flexible (high vinyl stearate content).

The copolymers can be cured with polyamines to infusible and insoluble materials. The copolymers having high vinyl stearate contents retain much of their flexibility after cure. Addition of carbon black or silica produces a reinforced plastic that can also be cured.

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